The electronic structure of oxo-Mn(salen): Single-reference and multireference approaches

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The electronic structure of oxo-Mn(salen): Single-reference and multireference approaches

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Using single- and multireference approaches we have examined many of the low-lying electronic states of oxo-Mn(salen), several of which have not been explored previously. Large complete-active-space self-consistent-field (CASSCF) computations have been performed in pursuit of an accurate ordering for the lowest several electronic states. Basis set and relativistic effects have also been considered. For the geometry considered, our best results indicate the ground spin state to be a closed-shell singlet, followed by a pair of low-lying triplet states, with additional singlet states and the lowest quintet state lying significantly higher in energy. Hartree-Fock and density functional theory (DFT) results are obtained and are compared to the more robust CASSCF results. The Hartree-Fock results are qualitatively incorrect for the relative energies of the states considered. Popular density functionals such as BP86 and B3LYP are superior to Hartree-Fock for this problem, but they give inconsistent answers regarding the ordering of the lowest singlet and triplet states and they greatly underestimate the singlet-quintet gap. We obtained multiple Hartree-Fock and DFT solutions within a given spin multiplicity, and these solutions have been subjected to wave function stability analysis. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2187974]

I. INTRODUCTION

The class of [O,N,N,O] tetradentate Schiff base complexes referred to as salen or salen-type ligands has seen numerous applications in transition metal catalysis.[1–3] This is due to their inherent ability to stabilize a number of different metals in various oxidation states and their amazing ability to transmit stereochemical information into the catalytic process.[3] Of these, the chiral manganese salen catalysts originally employed by Katsuki[4] and Jacobsen[5] for the asymmetric epoxidation of olefins have seen a great deal of attention in the literature[6] and they afford very high enantiomeric excess and yields.[5] Asymmetric epoxidation reactions have emerged as one of the most important synthetic tools developed in the past 30 years for the pharmaceuticals and fine-chemicals industries, contributions that were acknowledged in the awarding of the 2001 Nobel prize in chemistry.[7]

Numerous theoretical studies over the past decade have sought to elucidate the electronic properties that give rise to the stereochemical control afforded by the Mn(salen) system,[8–27] including extremely insightful works by Musaev, Morokuma, and co-workers[16,19,24,25,27] and by Cavallo and Jacobsen.[12,13,15,17,18,22,26] In order to undertake such studies these authors employ some model system that they expect to mimic the properties of the real system; some of the most common model systems are depicted in Fig. 1. Despite a large number of theoretical studies, however, extracting definitive conclusions from theory has proven challenging. For example, it has been noted that there exist major qualitative discrepancies in the description of the epoxidation reaction catalyzed by this system when comparing the two most commonly used density functionals.[17]

Manganese is one of the 3*d* metals, which have proven to be extremely challenging for electronic structure theory.[28] Indeed, both the Mn dimer[29] and the cationic MnO^+ (Ref. 30) are particularly difficult for standard theoretical methods. The spatial proximity of the 3*s*, 3*p*, and 3*d* orbitals gives rise to destabilizing effects for metal-ligand interactions that result in poor overlap between the 3*d* and ligand orbitals. This gives rise to orbital near degeneracies and a considerable amount of nondynamical correlation.[31] The ability of density functional theory (DFT) based approaches to adequately describe these long-range correlation effects remains an open question. The separation of the *nd* orbitals from the *ns* and

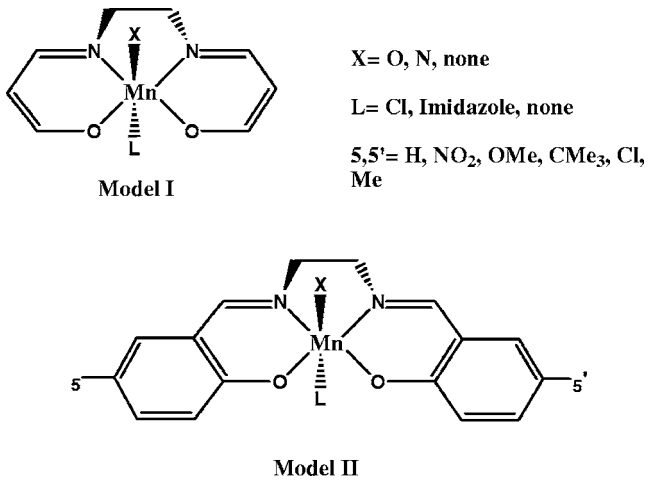

FIG. 1. Model systems for the Mn(salen) catalysts.

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np orbitals in 4*d* and 5*d* systems results in reduced nondynamical correlation effects and improved performance for standard theoretical approaches,[32] where relativistic effects are easily incorporated using effective core potentials.[33]

Concomitant with the difficulties of nondynamical correlation effects, systems containing 3*d* metals can feature several low-lying excited states of various multiplicities which give rise to surface crossing effects. The effect of intersystem crossings on chemical reactions involving heavier elements, where spin-orbit coupling effects may be large, has long been a matter of debate. Such reactions are often referred to as "spin-forbidden" processes because at zeroth-order spin-state changes are not allowed. However, it has been well demonstrated that such a view is too simplistic.[34] Indeed, extremely fast reactions may occur in transition metal containing systems despite being spin forbidden in nature.[35] A detailed understanding of the energies and geometries of reactants, products, intermediates, and minimum energy crossing points is often required to account for chemical reactivity and selectivity. Despite a number of theoretical studies, such a detailed picture of Mn(salen) catalyzed olefin epoxidation reactions remains elusive.

Since the pioneering work of Kohn and Sham,[36] DFT has emerged as an invaluable tool in computational chemistry for exploring the ground-state properties of molecular systems. In the Kohn-Sham formulation, the electron density is represented by a single Slater determinant. Such implementations of DFT should not be expected to be accurately applied to systems which are inherently multiconfigurational. Becke has commented that nondynamical correlation effects are at best accidently captured by LSDA, GGA, and "hybrid" DFT functionals.[37] Although the problems associated with applying current formalisms of DFT to multiconfigurational states have long been recognized,[38,39] the extension of DFT to the description of such states remains an active area of research.[40–50]

DFT results can be sensitive to the choice of functional (and this is particularly true for the current system). Indeed, numerous functionals have been developed for vastly different applications. Of these, the hybrid B3LYP is probably the most widely applied,[51] although its applicability should certainly not be considered universal. B3LYP has been shown to give rather poor estimates for spin-state splittings of many first-row transition metal dimers.[29] Indeed, a detailed analysis of the low-spin/high-spin splittings in a series of first-row transition metal dimers demonstrates the strong dependence upon the amount of "exact" exchange and supports decreasing the a_0 parameter to 0.15.[52] However, other authors have supported increasing the same parameter to as much as 0.50 to achieve improved performance for energy barriers.[53] When experimental data are scarce, one must rely upon high-level *ab initio* results to verify the applicability of DFT to a particular class of systems. Although this has been attempted for Mn(salen) systems with high-level coupled cluster (CC) studies,[14] the results have been disputed.[16,27] The only remaining high-level theoretical results have been the complete-active-space self-consistent-field (CASSCF) and multireference perturbation theory[54,55] (MRMP2) results presented by Ivanic *et al.*[23] Because the CASSCF method is capable of describing the nondynamical correlation effects in the oxo-Mn(salen) system, and because subsequent dynamical correlation effects have been shown by Ivanic *et al.* to be minor,[23] we have pursued expanded CASSCF studies here in an attempt to obtain a definitive ordering of the lowest singlet, triplet, and quintet states of the system. The sensitivity of the CASSCF results to the basis set has been examined along with a possible truncation of the active space from the study of Ivanic *et al.* Additionally, CASSCF wave functions are used to explore low-lying excited singlet and triplet states which have not previously been considered.

Finally, we explore the possibility of multiple solutions to the Hartree-Fock (HF) and Kohn-Sham DFT equations. In such self-consistent-field (SCF) based approaches a solution is iteratively sought such that the energy functional is stationary with respect to variation of the spin-orbitals. However, convergence to even a local minimum is not ensured by establishing zero first-order variation in the energy functional.[56] A necessary criterion for ensuring convergence to a local minimum is the positive definiteness of the orbital Hessian, the second-order changes of the energy functional with respect to infinitesimal variations of the orbitals. When there exists one or more negative eigenvalues of the orbital Hessian, the SCF solution is unstable with respect to variations of the spin-orbitals. This implies that there exists a lower-energy solution to the SCF equations, although this may not necessarily be the desired solution. The orbital instabilities can be classified into various types, some of which may result in solutions which break some of the employed constraints on the wave function.[57,58] The orbital-instability problems give rise to symmetry breaking for many simple molecular systems.[59–62] Ensuring convergence to a global minimum is extremely challenging even for the smallest of systems.[63] In this study, we have examined the existence of multiple solutions and wave function orbital instabilities for several commonly used SCF approaches as an attempt to understand some of the apparent discrepancies in the literature.

II. THEORETICAL METHODS

The model system and geometry were taken from previous work by Ivanic *et al.*[23] A 6-31G* basis[64–67] was employed for most of the computations. Additionally, some CASSCF wave functions were obtained using a larger basis which consisted of the 6-311G* basis[68,69] for all atoms except Mn, for which the augmented triple-zeta atomic natural orbital basis of Widmark *et al.*[70] was employed. These two choices of basis will be referred to as 6-31G* and 6-311G*, resulting in 273 and 423 contracted Gaussian functions, respectively.

Wave function stability analysis was performed within the computational chemistry package QCHEM 2.1.[71] Along with Hartree-Fock methods, several combinations of popular exchange[72,73] and correlation[74,75] functionals were employed. In order to examine the existence of multiple solutions and orbital instabilities, three separate calculations were performed for each spin state, each with a different set of initial guess orbitals. Initial guesses were generated using the core

Hamiltonian, using a superposition of atomic densities, and using the generalized Wolfsberg-Helmholtz (GWH) procedure.[76] In all cases, the SCF orbital optimization was performed using geometric direct minimization (GDM).[77] Although GDM is slightly more expensive than Pulay's direct inversion of the iterative subspace (DIIS),[78,79] the ability to take nonlinear steps in orbital rotation space provides more stable convergence for difficult systems. Convergence of a solution was assumed when the rms orbital gradient was less than 10^{-8}. The stability of each converged wave function was checked by diagonalization of the molecular orbital Hessian, and the type of instability present was analyzed. Hessian eigenvalues were assumed to be converged when the maximum deviation was less than 10^{-6}.

State-averaged complete-active-space self-consistent-field[80] (SA-CASSCF) calculations were performed with MOLPRO.[81] Two choices of active space were employed and will be discussed further below. Although previous results have indicated that the relativistic effects are likely quite small,[23] their impact has been explored by employing the perturbational Cowan-Griffin (CG) operator.[82] The CG relativistic corrections were computed at the SA-CASSCF level of theory in the 6-31G* basis.

III. RESULTS AND DISCUSSION

A. CASSCF computations and electronic state ordering

SA-CASSCF/6-31G* wave functions were obtained both with a 12 electron in 11 orbital active space as well as an 8 electron in 7 orbital active space. The former has been advocated by previous authors[23] and the latter was chosen after an examination of unrestricted Hartree-Fock (UHF) natural orbital (NO) occupation numbers.[83] The smaller active space consists of the $d[xy]$-(Mn), $\sigma(\mathrm{Mn}-\mathrm{O}_{ax})$, $\pi_1(\mathrm{Mn}-\mathrm{O}_{ax})$, and $\pi_2(\mathrm{Mn}-\mathrm{O}_{ax})$ occupied molecular orbitals along the the correlating orbitals $\sigma^*(\mathrm{Mn}-\mathrm{O}_{ax})$, $\pi_1^*(\mathrm{Mn}-\mathrm{O}_{ax})$, and $\pi_2^*(\mathrm{Mn}-\mathrm{O}_{ax})$. The larger active space is formed from the smaller by the addition of the two three-center–two-electron C–C–C-type π orbitals from the salen ligand ($R\pi_1$ and $R\pi_2$) along with the corresponding correlating orbitals $R\pi_1^*$ and $R\pi_2^*$. All of these orbitals are depicted in Fig. 2 from a CASSCF/6-31G*(12/11) calculation of the $1\,^5A$ state.

In the study of Ivanic *et al.*,[23] a triplet ground state is predicted for the oxo-Mn(salen) model system. The singlet was predicted to be a few kcal mol^{-1} higher in energy followed by the quintet at approximately 40 kcal mol^{-1}. However, the authors were unable to converge the CASSCF(12/11) wave function for the singlet state. The problem stemmed from a weakly occupied $d[xy]$-(Mn) orbital in the active space that rotated with a chlorine core orbital. This led the authors to place the d orbital into the restricted space, performing a CASSCF(10/10) calculation. To allow for a comparison of relative energies after the orbitals were converged, the authors then performed an Edminston-Ruedenberg[84] (ER) localization of the restricted-space orbitals and placed the d orbital back into the active space, performing a CAS-CI(12/11) computation.

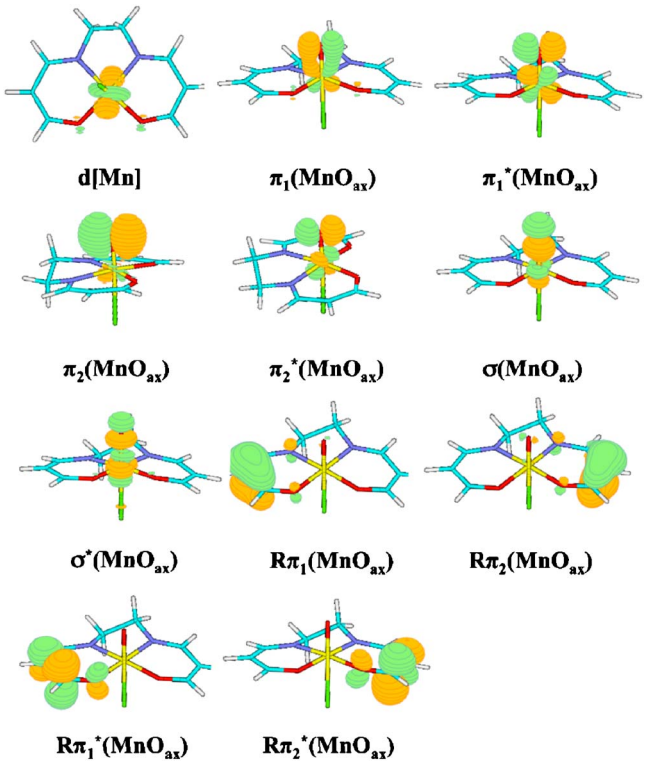

FIG. 2. CASSCF/6-31G* natural orbitals for the $1\,^5A$ state of oxo-Mn(salen).

The study of Ivanic *et al.* employed modified virtual orbitals[85] from a HF calculation as initial guess orbitals for the CASSCF. Here, the starting orbitals were the natural orbitals from a CASSCF(12/11) calculation in a STO-3G basis.[86,87] In turn, the CASSCF/STO-3G computations used the natural orbitals of a CI singles and doubles computation as a guess. Using this procedure, we were able to converge the CASSCF(12/11) calculations for the singlet state while avoiding the rotation of the d orbital out of the active space. The resulting CASSCF(12/11) total and relative energies for the $1\,^1A$, $1\,^3A$, and $1\,^5A$ states are presented in Table I along with the CAS-CI energy of Ivanic *et al.* As can be seen from the table, the energy of the $1\,^1A$ drops below that of the $1\,^3A$ state when using a converged CASSCF solution. The converged CASSCF energy of the $1\,^1A$ state lies a little more than 3 kcal mol^{-1} lower than the CAS-CI energy of Ivanic *et al.* From these calculations, the singlet and triplet states are predicted to be essentially degenerate, with a singlet ground state followed by the triplet less than 0.5 kcal mol^{-1} higher in energy. The quintet remains around 40 kcal mol^{-1}

TABLE I. Total (hartree) and relative (kcal mol^{-1}) energies for three electronic states of oxo-Mn(salen).

State	Total energy	Relative energy
$1\,^1A$ CASSCF(12/11)/6-31G*	−2251.430 527[a]	0.00
$1\,^1A$ CAS-CI(12/11)/6-31G*	−2251.425 50[b]	3.15
$1\,^3A$ CASSCF(12/11)/6-31G*	−2251.430 11[b]	0.26
$1\,^5A$ CASSCF(12/11)/6-31G*	−2251.362 20[b]	42.88

[a]This work.
[b]Reference 23.

higher in energy. The approach presented above for generating starting orbitals for the CASSCF calculation was employed for all of the remaining calculations unless otherwise stated.

One of the major sources of difficulty in computational studies of this system has been the number and proximity of many low-lying excited states. In order to gain an understanding of the qualitative ordering of these states, we initially performed CAS-CI calculations for several roots on each of the spin manifolds using the converged orbitals from the CASSCF/6-31G*(12/11) calculation of the $1\,^5A$ state. These calculations indicate that two triplet states and the closed-shell singlet state are nearly degenerate in energy. Lying slightly higher in energy are two open-shell singlet states followed by the high-spin quintet $1\,^5A$. These six lowest electronic states that are capable of being described by the current active spaces have been studied extensively in this work and will be tentatively labeled $1\,^1A$, $2\,^1A$, $3\,^1A$, $1\,^3A$, $2\,^3A$, and $1\,^5A$. Preliminary studies indicate that other states capable of being described with this active space lie higher in energy and were not considered further. It should be noted that only three of these states (the lowest singlet, triplet, and quintet) have been considered previously by other authors and it is unclear at this stage what impact the presence of these low-lying excited states will have on the chemistry of this system.

The SA-CASSCF method has been shown to provide a reliable reference for vertical excitation energies in some systems[88] as it affords a balanced description of the relevant electronic states. However, one important consideration when performing such calculations is how to average over the electronic states. There are inherent advantages and disadvantages both to averaging over more and to averaging over fewer of the states of a given system. The states included in a SA-CASSCF calculation are orthogonal by construction and must be described by a common set of molecular orbitals. Averaging over fewer states in a given calculation will certainly provide more flexibility in the description of the electronic states, but may lead to erroneous root-flipping problems for states that lie close in energy. Averaging over more states will lead to fewer calculations required to obtain the desired excitation energies and fewer root-flipping problems, but the primary consideration now is whether all of the electronic states can be accurately described by a common set of molecular orbitals. If this is the case, it may be possible to reliably obtain all of the excitation energies of interest from a single calculation.

In the present study, we have obtained SA-CASSCF wave functions using three different averaging schemes. In the most flexible approach considered, SA-CASSCF wave functions were obtained from four separate calculations including (a) the $1\,^1A$ state, (b) the $2\,^1A$ and $3\,^1A$ states, (c) the $1\,^3A$ and $2\,^3A$ states, and (d) the $1\,^5A$ state. This will be conveniently represented with the following notation $[1\,^1A/2\,^1A,3\,^1A/1\,^3A,2\,^3A/1\,^5A]$. The total and relative energies are presented in Table II. Both sets of calculations predict the ground spin state to be the $1\,^1A$ state, in contrast to the triplet state found by Ivanic. Only slightly higher in energy are the nearly degenerate $1\,^3A$ and $2\,^3A$ states. A nearly degenerate pair of open-shell singlet states, $2\,^1A$ and $3\,^1A$, is found around 35 kcal mol^{-1} followed by the $1\,^5A$ state above 40 kcal mol^{-1}. Single-state CASSCF calculations attempted on the $3\,^1A$ and the $2\,^3A$ states resulted in root-flipping problems and could not be converged. It is extremely promising that the results from the two active spaces [(12/11) and (8/7)] are very similar. The relative energies differ by less than 0.5 kcal mol^{-1} for all of the states except the high-lying $1\,^5A$ state, for which the difference is only 1.4 kcal mol^{-1}.

TABLE II. Total (hartree) and relative (kcal mol^{-1}) SA-CASSCF/6-31G* ($1\,^1A/2\,^1A,3\,^1A/1\,^3A,2^3A/1\,^5A$) energies for the relevant electronic states of oxo-Mn(salen).

	SA-CASSCF(12/11)		SA-CASSCF(8/7)	
State	Total energy	Relative energy	Total energy	Relative energy
$1\,^1A$	−2251.430 527	0.00	−2251.401 094	0.00
$2\,^1A$	−2251.376 300	34.03	−2251.346 203	34.44
$3\,^1A$	−2251.373 073	36.05	−2251.343 313	36.26
$1\,^3A$	−2251.427 234	2.07	−2251.397 173	2.46
$2\,^3A$	−2251.426 278	2.67	−2251.396 381	2.96
$1\,^5A$	−2251.362 197	42.88	−2251.330 493	44.30

The second state-averaging approach, $[1\,^1A,2\,^1A,3\,^1A/1\,^3A,2\,^3A/1\,^5A]$, averages separately over each of the spin manifolds, requiring three separate calculations. The only impact this has on the energies is upon the singlet states, which are now required to be orthogonal and described by a common set of orbitals. The total and relative energies are presented in Table III. From the results we see that, by averaging over all of the singlet states, we have significantly raised the energy of the $1\,^1A$ state. This could either be the result of requiring a common set of molecular orbitals or the result of the imposed orthogonality of the singlet states. A closer examination of the results implies that the effect is most likely the result of the imposed orthogonality. The energies of the $2\,^1A$ and $3\,^1A$ states are much less affected by the changes, the increase in total energy being an order of magnitude less for these states than for the $1\,^1A$ state.

The final averaging scheme, $[1\,^1A,2\,^1A,3\,^1A,1\,^3A,2\,^3A,1\,^5A]$, attempts six states from a single CASSCF. The total and relative energies are presented in Table IV. This averaging scheme imposes no additional orthogonality con-

TABLE III. Total (hartree) and relative (kcal mol^{-1}) SA-CASSCF/6-31G* $[1\,^1A,2\,^1A,3\,^1A/1\,^3A,2\,^3A/1\,^5A]$ energies for the relevant electronic states of oxo-Mn(salen).

	SA-CASSCF(12/11)		SA-CASSCF(8/7)	
State	Total energy	Relative energy	Total energy	Relative energy
$1\,^1A$	−2251.424 606	1.65	−2251.395 150	1.27
$2\,^1A$	−2251.375 485	32.47	−2251.345 394	32.49
$3\,^1A$	−2251.372 129	34.58	−2251.342 357	34.40
$1\,^3A$	−2251.427 234	0.00	−2251.397 173	0.00
$2\,^3A$	−2251.426 278	0.60	−2251.396 381	0.63
$1\,^5A$	−2251.362 197	40.81	−2251.330 493	41.84

TABLE IV. Total (hartree) and relative (kcal mol^{-1}) SA-CASSCF/6-31G* [$1\,^1A, 2\,^1A, 3\,^1A, 1\,^3A, 2\,^3A, 1\,^5A$] energies for the relevant electronic states of oxo-Mn(salen) using a 6-31G* basis.

	SA-CASSCF(12/11)		SA-CASSCF(8/7)	
State	Total energy	Relative energy	Total energy	Relative energy
$1\,^1A$	−2251.419 298	4.15	−2251.389 802	3.79
$2\,^1A$	−2251.374 790	32.08	−2251.344 722	32.08
$3\,^1A$	−2251.372 001	33.83	−2251.342 249	33.63
$1\,^3A$	−2251.425 905	0.00	−2251.395 843	0.00
$2\,^3A$	−2251.424 670	0.78	−2251.394 843	0.63
$1\,^5A$	−2251.352 430	46.11	−2251.320 483	47.29

straints on the system as the states of different spin symmetries are orthogonal by construction. As such, the predicted relative energies are changed only slightly in comparison with those from the SA-CASSCF [$1\,^1A, 2\,^1A, 3\,^1A/1\,^3A, 2\,^3A/1\,^5A$] results presented in Table III. Both approaches predict the ground state to be characterized by a pair of nearly degenerate triplet states, followed by a low-lying closed-shell singlet state. These results clearly demonstrate that the ordering of the relevant electronic states depends strongly upon the choice of averaging schemes. However, it is indeed promising that the smaller active space gives results consistent with those from the larger active space.

A molecular orbital diagram of the most important orbitals is presented in Fig. 3. The ground state of the system, $1\,^1A$ (at least according to our most flexible SA-CASSCF averaging scheme) corresponds to the closed-shell configuration $\sigma(\mathrm{Mn-O}_{ax})^2\pi_1(\mathrm{Mn-O}_{ax})^2\pi_2(\mathrm{Mn-O}_{ax})^2\mathrm{d[xy]}^2$. The $1\,^3A$ and $2\,^3A$ states and the open-shell $2\,^1A$ and $3\,^1A$ states correspond to $\mathrm{d[xy]} \rightarrow \pi^*(\mathrm{Mn-O}_{ax})$ excitations. It is interesting to note the extent to which the $\pi(\mathrm{Mn-O}_{ax})$ and the $\pi^*(\mathrm{Mn-O}_{ax})$ pairs of molecular orbitals are split. This leads to a slight splitting of the triplet states which is magnified in the pair of open-shell singlet states (approximately 2 kcal mol^{-1}). This is further exemplified by the CI coefficients for the two states. The coefficients for the

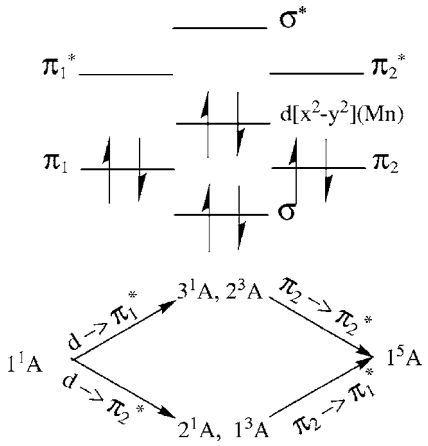

FIG. 3. Diagram of the key orbitals in the description of the low-lying electronic states of oxo-Mn(salen). Below these are the dominant excitations that lead to the excited states from the closed-shell $1\,^1A$ ground state.

$\mathrm{d[xy]}\alpha\pi_1^*(\mathrm{Mn-O}_{ax})\alpha$ and the $\mathrm{d[xy]}\alpha\pi_2^*(\mathrm{Mn-O}_{ax})\alpha$ configurations are 0.14 and 0.85 for the $1\,^3A$ state and 0.85 and −0.14 for the $2\,^3A$ state. The $1\,^5A$ state corresponds to a $\pi(\mathrm{Mn-O}_{ax}) \rightarrow \pi^*(\mathrm{Mn-O}_{ax})$ excitation from the triplet states. Again, it is interesting to note that the leading configuration is $\sigma^2\pi_2^2d^1\pi_1^1\pi_1^{*1}\pi_2^{*1}$, with a weight of 0.96. The corresponding $\sigma^2\pi_1^2d^1\pi_2^1\pi_1^{*1}\pi_2^{*1}$ configuration has a weight of less than 0.05.

The largest error in the CASSCF computations might be thought to be the lack of dynamical electron correlation, which is captured only indirectly in CASSCF, but may be included explicitly via CASPT2 or other multi-reference methods. Previous work by Ivanic using the multi-reference MP2 (MRMP2) method[23] indicates that the effect of dynamical correlation is rather small (contributing 0.6 and 5.5 kcal mol^{-1} respectively to the relative energies of the $1\,^3A$ and $1\,^5A$ states), in both cases increasing the energy relative to the $1\,^1A$ state. This is consistent with the observations that closed-shell systems exhibit larger dynamical correlation effects and thus tend to be overestimated energetically at the CASSCF level.[89] The next most important source of error might be the basis set. It is well known that wave function based approaches are typically slower to converge with respect to basis set than DFT based approaches. We have investigated the basis set convergence of the relative SA-CASSCF energies using a 6-311G* basis set. The SA-CASSCF/6-311G*[$1\,^1A/2\,^1A, 3\,^1A/1\,^3A, 2\,^3A/1\,^5A$] and SA-CASSCF/6-311G*[$1\,^1A, 2\,^1A, 3\,^1A, 1\,^3A, 2\,^3A, 1\,^5A$] total energies are presented in Tables V and VI, respectively, along with the changes in total and relative energies for the various electronic states. The results indicate that basis set effects may indeed be more important for determining the ground spin state of the system than are the effects of dynamical correlation. In the most flexible averaging scheme, increasing the size of the basis raises the relative energies of all of the triplet and open-shell singlet states by approximately 1.2 kcal mol^{-1}, with the relative energy of the $1\,^5A$ state increasing by only 0.39 kcal mol^{-1}. Although the more restrictive, [$1\,^1A, 2\,^1A, 3\,^1A, 1\,^3A, 2\,^3A, 1\,^5A$], choice of averaging does not reproduce the proper ordering of the electronic states, the $1\,^1A$ and $1\,^5A$ states are still stabilized relative to the triplet states upon going to the larger basis. Finally, even though none of the atoms are particularly heavy, one might suppose that relativistic effects could be significant due to the Mn atom. Ivanic *et al.* examined the importance of relativistic effects on the electronic state ordering of this system by comparing all-electron calculations to those employing a relativistic effective core potential.[23] Although the results indicated that the relativistic effects were negligible for determining the electronic state ordering, we have examined the importance of such effects using the Cowan-Griffin relativistic correction to the all-electron calculations. The results are presented in Table VII. From the results one can see that, although the relativistic corrections to the total energies are quite large, the contribution of the relativistic effects to the relative energies is typically less than 0.1 kcal mol^{-1}.

Of primary importance when considering the applicability of single-reference based electronic structure theories to

TABLE V. Total energies (hartree) at the SA-CASSCF/6-311G* [$1\,^1A/2\,^1A,3\,^1A/1\,^3A,2\,^3A/1\,^5A$] level of theory and changes in total energies (hartree) and relative energies (kcal mol^{-1}) due to the basis set expansion from 6-31G* to 6-311G* for the relevant electronic states of oxo-Mn(salen).

	SA-CASSCF(12/11)			SA-CASSCF(8/7)		
State	Total energy	ΔE_{tot}	ΔE_{rel}	Total energy	ΔE_{tot}	ΔE_{rel}
$1\,^1A$	−2251.745 514	−0.314 987	0.0	−2251.715 642	−0.314 548	0.00
$2\,^1A$	−2251.689 302	−0.313 002	1.24	−2251.658 787	−0.312 584	1.24
$3\,^1A$	−2251.686 166	−0.313 094	1.19	−2251.655 956	−0.312 643	1.19
$1\,^3A$	−2251.740 367	−0.313 133	1.16	−2251.709 875	−0.312 702	1.16
$2\,^3A$	−2251.739 428	−0.313 150	1.15	−2251.709 073	−0.312 692	1.16
$1\,^5A$	−2251.676 429	−0.314 231	0.47	−2251.644 424	−0.313 931	0.39

the current problem is the multireference nature of the electronic wave function. For each state, Table VIII presents the contribution (CI coefficient) in the CASSCF NO basis for all determinants with a coefficient of 0.15 or larger. The results show that the triplet states are highly multireference, with the leading determinant in each case capturing only about 72% of the total wave function. A single-determinant description is not expected to be applicable for the open-shell singlet states. However, the leading pair of determinants (the smallest number of determinants capable of describing the open-shell wave function) capture only about 77% of the total wave function for each of these states. This may be contrasted with CASSCF wave functions for the ground state of well-behaved systems. For the H_2O molecule in an aug-cc-pVDZ basis set near its equilibrium geometry ($R=1.843\,45$ bohr, $\Theta=110.60$), the leading closed-shell determinant captures 96% of the CASSCF wave function using a valence active space and a CASSCF-NO basis (the second leading configuration contributes less than 1%). The coefficient of the leading determinant of the closed-shell $1\,^1A$ state of our Mn(salen) model system, 0.90, is larger than that for the triplet states but is still smaller than what one might expect for a well-behaved single-reference system. The $1\,^5A$ state, with a leading coefficient of 0.96, appears to be the most highly single-reference of the states considered. It is clear from the CI coefficients that the triplet and singlet states are highly multireference in nature. As such, accurate relative energies for these states should not be expected from single-reference approaches.

The most accurate calculations presented here, employing large basis sets and relativistic corrections, predict the ground state to be the closed-shell $1\,^1A$ state. Lying slightly more than 3 kcal mol^{-1} higher in energy is a pair of nearly degenerate triplet states. A pair of open-shell singlet states lies above 30 kcal mol^{-1}, with the $1\,^5A$ state at greater than 40 kcal mol^{-1}. It is anticipated that corrections for dynamical correlation and finite basis sets will tend to stabilize the lowest closed-shell singlet state relative to the other states.

B. Single-reference approaches

As noted above, there exist major discrepancies in the description of the asymmetric epoxidation reaction catalyzed by oxo-Mn(salen) when using two of the most commonly employed density functionals. In Table IX we present the relative energies for the various electronic states from several restricted Kohn-Sham (RKS) and restricted open-shell Kohn-Sham (ROKS) approaches as well as restricted and restricted open-shell Hartree-Fock (RHF/ROHF). Comparing BP86 to BLYP and B3P86 to B3LYP, it is obvious that the spin-state splittings are largely insensitive to the choice of correlation functional. Both B3LYP and B3P86 predict the ground state to be the $1\,^3A$ state followed by the closed-shell singlet at 2–3 kcal mol^{-1}. The quintet is predicted to be less than 20 kcal mol^{-1} above the triplet. Both BP86 and BLYP predict the closed-shell $1\,^1A$ state to be the ground state, with the $1\,^3A$ state around 1–2 kcal mol^{-1}. The quintet is predicted to lie a little more than 20 kcal mol^{-1} higher in energy. It is clear from the results that the hybrid functionals (B3LYP and B3P86) stabilize the high-spin states relative to the nonhy-

TABLE VI. Total energies (hartree) at the SA-CASSCF/6-311G* [$1\,^1A,2\,^1A,3\,^1A,1\,^3A,2\,^3A,1\,^5A$] level of theory and changes in total energies (hartree) and relative energies (kcal mol^{-1}) due to basis set expansion from 6-31G* to 6-311G* for the relevant electronic states of oxo-Mn(salen).

	SA-CASSCF(12/11)			SA-CASSCF(8/7)		
State	Total energy	ΔE_{tot}	ΔE_{rel}	Total energy	ΔE_{tot}	ΔE_{rel}
$1\,^1A$	−2251.732 704	−0.313 406	−0.23	−2251.732 704	−0.313 406	−0.23
$2\,^1A$	−2251.687 477	−0.312 687	0.22	−2251.687 477	−0.312 687	0.22
$3\,^1A$	−2251.684 653	−0.312 652	0.24	−2251.684 653	−0.312 652	0.24
$1\,^3A$	−2251.738 948	−0.313 043	0.00	−2251.738 948	−0.313 043	0.00
$2\,^3A$	−2251.737 650	−0.312 980	0.04	−2251.737 650	−0.312 980	0.04
$1\,^5A$	−2251.666 479	−0.314 050	−0.63	−2251.666 479	−0.314 050	−0.63

TABLE VII. Cowan-Griffin relativistic corrections (hartree) to the energy of the electronic states of oxo-Mn(salen) computed at the SA-CASSCF(12/11)/6-31G* level of theory and their contribution to the relative energies (kcal mol^{-1}).

State	E_{rel}	ΔE
$1\,^1A$	−9.115 630	0.01
$2\,^1A$	−9.115 772	−0.08
$3\,^1A$	−9.115 768	−0.08
$1\,^3A$	−9.115 645	0.00
$2\,^3A$	−9.115 638	0.00
$1\,^5A$	−9.116 107	−0.29

brid approaches (BLYP and BP86). There are a few things to note with respect to the RHF/ROHF results. Exchange terms due to the Pauli exclusion principle result in dramatic overstabilization of the high-spin states. The spin-state stability increases with increasing spin multiplicity, predicting the quintet to be the lowest of the three spin states considered, followed by the triplets and then the singlets. Indeed, a ROHF calculation on the septet state predicts this to be even lower than the quintet by almost 30 kcal mol^{-1}. It is also interesting that there exist multiple solutions to the HF equations for each of the spin multiplicities, differing at one point by more than 15 kcal mol^{-1} in energy. It should also be mentioned that all of the RHF/RKS singlet states exhibit large restricted-unrestricted orbital instabilities, although the negative orbital Hessian eigenvalues are smaller in magnitude for DFT approaches ($|\epsilon| < 0.05$) than for HF ($|\epsilon| > 0.25$). Following these instabilities leads to slightly spin-contaminated unrestricted Kohn-Sham (UKS) solutions and a highly spin-contaminated UHF solution as discussed below. We are currently unable to perform stability analysis on the ROHF/ROKS wave functions.

TABLE VIII. Leading configurations in the description of the low-lying electronic states of oxo-Mn(salen) computed at the SA-CASSCF(8/7)/6-31G* [$1\,^1A/2\,^1A, 3\,^1A/1\,^3A, 2\,^3A/1\,^5A$] level of theory.

State	Configuration	Coefficient
$1\,^1A$	$(d)^2(\sigma)^2(\pi_1)^2(\pi_2)^2$	0.90
	$(d)^2(\sigma)^2(\pi_1)^2(\pi_2^*)^2$	−0.18
	$(d)^2(\sigma)^2(\pi_2)^2(\pi_1^*)^2$	0.17
$2\,^1A$	$(\sigma)^2(\pi_1)^2(\pi_2)^2(d)\alpha(\pi_2^*)\beta$	0.62
	$(\sigma)^2(\pi_1)^2(\pi_2)^2(d)\beta(\pi_2^*)\alpha$	−0.62
	$(\sigma)^2(\pi_2)^2(\pi_1^*)^2(d)\alpha(\pi_2^*)\beta$	−0.15
	$(\sigma)^2(\pi_2)^2(\pi_1^*)^2(d)\beta(\pi_2^*)\alpha$	0.15
$3\,^1A$	$(\sigma)^2(\pi_1)^2(\pi_2)^2(d)\alpha(\pi_1^*)\beta$	0.62
	$(\sigma)^2(\pi_1)^2(\pi_2)^2(d)\beta(\pi_1^*)\alpha$	−0.62
	$(\sigma)^2(\pi_2)^2(\pi_1^*)^2(d)\alpha(\pi_1^*)\beta$	−0.15
	$(\sigma)^2(\pi_2)^2(\pi_1^*)^2(d)\beta(\pi_1^*)\alpha$	0.15
$1\,^3A$	$(\sigma)^2(\pi_1)^2(\pi_2)^2(d)\alpha(\pi_2^*)\alpha$	0.85
	$(\sigma)^2(\pi_2)^2(\pi_1^*)^2(d)\alpha(\pi_2^*)\alpha$	−0.24
	$(\sigma)^2(\pi_2)^2(\pi_1)\beta(d)\alpha(\pi_1^*)\alpha(\pi_2^*)\alpha$	−0.22
	$(\sigma)^2(\pi_2^*)^2(\pi_1)\beta(\pi_2)\alpha(d)\alpha(\pi_1^*)\alpha$	0.15
$2\,^3A$	$(\sigma)^2(\pi_1)^2(\pi_2)^2(d)\alpha(\pi_1^*)\alpha$	0.85
	$(\sigma)^2(\pi_1)^2(\pi_2^*)^2(d)\alpha(\pi_1^*)\alpha$	−0.24
	$(\sigma)^2(\pi_1)^2(\pi_2)\beta(d)\alpha(\pi_1^*)\alpha(\pi_2^*)\alpha$	0.22
	$(\sigma)^2(\pi_1^*)^2(\pi_2)\beta(\pi_1)\alpha(d)\alpha(\pi_2^*)\alpha$	−0.15
$1\,^5A$	$(\sigma)^2(\pi_2)^2(\pi_1)\alpha(d)\alpha(\pi_1^*)\alpha(\pi_2^*)\alpha$	0.96
	$(\pi_2)^2(\sigma^*)^2(\pi_1)\alpha(d)\alpha(\pi_1^*)\alpha(\pi_2^*)\alpha$	−0.16

TABLE IX. Energies (kcal mol^{-1}) relative to the lowest triplet state and wave function instabilities for restricted single-reference methods using a 6-31G* basis.

Method	State	Energy
B3LYP	Singlet	1.85
	Triplet	0.00
	Quintet	17.65
BP86	Singlet	−1.30
	Triplet	0.00
	Quintet	24.69
BLYP	Singlet	−1.99
	Triplet	0.00
	Quintet	23.65
B3P86	Singlet	2.92
	Triplet	0.00
	Quintet	13.67
B3LYP*	Singlet	0.82
	Triplet	0.00
	Quintet	15.38
HF	Singlet	41.33
	Singlet	41.39
	Triplet	15.31
	Triplet	0.00
	Quintet	−37.94
	Quintet	−38.10

Table X presents the relative energies, $\langle \hat{S}^2 \rangle$ values, and orbital Hessian eigenvalues of all stable and unstable solutions obtained using unrestricted single-reference approaches. Like RHF, UHF theory also results in a very unphysical description of the electronic state ordering. Indeed, the relative energies of the states considered are completely different than our best CASSCF results presented above. Like ROHF, UHF predicts a septet ground state, and it places the lowest quintet state 10 kcal mol^{-1} below the lowest singlet state, in contradiction to our best CASSCF prediction of a singlet ground state. However, the overstabilization of the quintet and septet is significantly reduced compared to the ROHF results. Concomitant with the very poor UHF relative energies, Table X indicates that the UHF wave functions are all highly spin contaminated. The UKS DFT solutions also exhibit spin contamination, although to a much smaller degree. Just as for ROKS, the UKS energies are much less sensitive to the choice of correlation functional than to the treatment of exchange. Additionally, the UKS relative energies are very similar to those obtained using ROKS (typically within 1 kcal mol^{-1}), the only exception being the B3LYLP results.

Table X indicates multiple UHF solutions, just as for ROHF. However, while we observed only one RKS/ROKS solution for each of the singlet, triplet, and quintet states, we observe additional high-spin solutions for unrestricted BP86,

TABLE X. Energies (kcal mol^{-1}) relative to the lowest triplet state and lowest eigenvalues of the orbital Hessian state and lowest eigenvalues of the orbital Hessian for unrestricted single-reference methods using a 6-31G* basis. (All negative eigenvalues of the molecular orbital Hessian included in this table were from UKS-CUKS orbital instabilities.)

Method	State	$\langle \hat{S}^2 \rangle$	Energy	Eigenvalues
B3LYP	^1A	0.52	3.53	0.004,0.033
	^3A	2.21	0.00	0.003,0.009
	^5A	6.04	11.94	0.007,0.013
	^7A	12.07	75.32	0.017,0.018
BP86	^1A	0.51	−1.87	0.007,0.033
	^3A	2.04	0.00	0.005,0.009
	^5A	6.02	29.46	−0.010,0.010
	^5A	6.02	24.18	0.006,0.011
	^7A	12.02	93.15	−0.003,0.005
	^7A	12.03	91.03	0.006,0.011
BLYP	^1A	0.47	−2.09	0.007,0.033
	^3A	2.04	0.00	0.005,0.010
	^5A	6.02	28.22	−0.010,0.011
	^5A	6.02	23.08	0.006,0.011
	^7A	12.02	91.71	−0.002,0.006
	^7A	12.03	89.81	0.005,0.013
B3P86	^1A	0.57	3.53	0.004,0.032
	^3A	2.21	0.00	0.003,0.008
	^5A	6.04	13.42	0.008,0.013
	^7A	12.07	77.48	0.016,0.017
B3LYP*	^1A	0.51	1.75	0.005,0.033
	^3A	2.10	0.00	0.004,0.008
	^5A	6.03	20.25	−0.011,0.005
	^5A	6.04	14.67	0.007,0.012
	^7A	12.06	81.09	0.007,0.008
HF	^1A	2.91	40.64	0.003,0.044
	^1A	2.33	14.92	0.003,0.026
	^3A	2.99	39.79	0.001,0.013
	^3A	3.28	0.00	0.001,0.013
	^3A	3.35	13.50	0.003,0.027
	^5A	6.03	27.91	0.001,0.013
	^5A	6.53	4.27	0.003,0.016
	^7A	13.16	10.20	0.017.0.085
	^7A	12.43	−2.32	0.003,0.012

BLYP, and B3LYP* (which has 15% HF exchange).[52] For the unrestricted wave functions, we were able to perform a stability analysis, and the lowest eigenvalues of the orbital Hessian are presented in the table. We find that the "extra" solutions found for UKS but not for ROKS all correspond to unstable wave functions (with negative orbital Hessian eigenvalues). Perhaps surprisingly, however, all of the UHF solutions we obtained are stable, indicating that they are local minima in orbital rotation space. One might suppose that the "wrong" UHF solutions would exhibit very small Hessian eigenvalues. However, from Table X we see that the smallest eigenvalues for these wrong solutions may be larger than those for the lowest-energy UHF solution. Given that these solutions are locally stable, it is not immediately clear how one would know whether such a high-lying solution had been obtained (short of a search for multiple solutions as we have done here). Furthermore, none of the procedures employed for generating the initial guess orbitals consistently provides for the correct SCF solution. The core Hamiltonian appears to be a rather poor initial guess for this particular system, and for the optimization procedures we employed, it always results in the UHF solution that is the highest in energy (of those we found) for the given multiplicity. Using a GWH guess would result in the correct singlet, triplet, and quintet UHF wave functions. However, one would land upon the higher septet result. The only guess to result in the correct septet UHF result was the superposition of atomic densities. However, this particular guess results in the wrong solution for all other states.

IV. CONCLUSIONS

We have examined several electronic states of the oxo-Mn(salen) model system, some of which have not been previously explored, using robust *ab initio* methods. SA-CASSCF/6-311G* calculations predict the closed-shell 1 ^1A state to be the ground spin state, with the 1 ^3A and 2 ^3A states slightly more than 3 kcal mol^{-1} higher in energy. Such a difference is within the potential errors of the calculations. However, it is anticipated that calculations incorporating larger basis sets and corrections for dynamical correlation will push the singlet state lower in energy relative to the triplets. A pair of nearly degenerate open-shell singlet states, 2 ^1A and 3 ^1A, lie around 35 kcal mol^{-1} followed by the high-spin 1 ^5A state at a little more than 40 kcal mol^{-1}. It is currently unclear what significance the presence of these previously unexplored electronic states may have in understanding the chemistry of this system. The proximity of so many states may result in highly complex potential energy surfaces involving conical intersections and avoided crossing effects. It is evident from this work that even a definitive determination of the ground spin state for this system will require very extensive treatments of electron correlation in conjunction with very large basis sets. As previously described by Ivanic *et al.*,[23] in the closed-shell singlet state, we observe triple-bond character between the manganese metal and the axial oxygen atom. Through detailed analysis of the CI expansion from CASSCF calculations, we have demonstrated the multireference character of this system. Much care should be taken when applying single-reference based approaches to such problems.

We have examined the applicability of several single-reference SCF approaches for describing the electronic structure of the current model system, while exploring the existence of multiple SCF solutions and their potential impact on previous theoretical studies. Hartree-Fock theory has been demonstrated to give an extremely poor description of this system and does not provide a reliable starting point for theoretical investigations. The existence of multiple SCF solutions and large spin-contamination effects in UHF based approaches makes the use of HF and even post-HF single-reference theories suspect. If one were to use standard single-reference approaches, such as the coupled-cluster theories employed by Abashkin *et al.*,[14] several potential problems could arise. First of all, there is the possibility that the HF

computation would land on a higher-energy solution which would then be employed as a starting point for the post-HF correlation model. Secondly, even the stable HF solutions provide a very unphysical description for the ordering and would require very large electron-correlation corrections.

These considerations may help explain the rather different energetics found by Abashkin *et al.*[14] using CC theory through perturbative triple excitations [CCSD(T)] with a polarized double-zeta basis and a similar model system: 0.0 (singlet), 14.5 (triplet), and 10.9 kcal mol^{-1} (quintet). It is unclear from the CCSD(T) total energies reported by these authors if they might have resulted from the use of higher-lying HF solutions. However, we note that these computations were performed using GAUSSIAN 98,[90] which uses a pseudoextended Huckel guess by default. A very interesting 1999 study by Vacek *et al.*[91] demonstrated that Huckel guess orbitals led to the lowest-energy HF wave function only 14% of the time for a set of 80 organometallic molecules. Hence, in the absence of further information, it is possible that the study by Abashkin *et al.*[14] may have used one of these higher-lying HF reference solutions. Assuming that the lowest-energy HF references were employed, the discrepancy between our CASSCF results and the CCSD(T) results may very well be a consequence of the multireference nature of the singlet and triplet states. Although the quintet state appears to be primarily single reference, the singlet and triplet states are clearly multireference. The lower relative energy of the $1\ ^5A$ state predicted by CCSD(T) may thus be the result of CC theory predicting too high a total energy for the singlet and triplet states, for which single-reference formalisms may not be applicable.

DFT approaches provide a much more physical description than does HF theory. Although all DFT approaches predict the lowest singlet and triplet states to lie very close in energy, the hybrid functionals stabilize the triplet state relative to the nonhybrid approaches. All functionals explored place the quintet state much lower in energy than predicted by the CASSCF method, with the hybrid functionals again stabilizing the high-spin states relative to the nonhybrid approaches. Again, this may very well be a result of the multireference nature of the singlet and triplet states. Although a few (unstable) SCF solutions were observed with some of the density functionals, we did not find as many DFT solutions as HF solutions. The nonhybrid approaches BP86 and BLYP give results that appear to be in better agreement with the CASSCF results (or with previous coupled-cluster results)[14] than the hybrid DFT approaches, but it would be difficult to advocate their superiority based solely upon the results presented here. It is clear from previous work that the choice of functional provides for qualitatively different results in mechanistic studies involving the current system.[17] A definitive answer as to what functional, if any, is capable of accurately describing the mechanisms of Mn(salen) catalyzed epoxidation reactions remains as yet unanswered.

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